



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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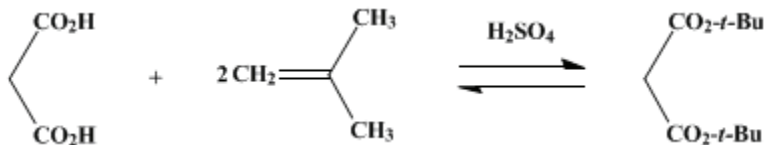
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.261 (1963); Vol. 34, p.26 (1954).

DI-*tert*-BUTYL MALONATE

[Malonic acid, di-*t*-butyl ester]

[I. ISOBUTYLENE METHOD]



Submitted by Allen L. McCloskey, Gunther S. Fonken, Rudolph W. Kluiber, and William S. Johnson¹.

Checked by James Cason, Gerhard J. Fonken, and William G. Dauben.

1. Procedure

A 500-ml. Pyrex heavy-walled narrow-mouthed pressure bottle is charged with 100 ml. of *ether* (Note 1), 5 ml. of concentrated *sulfuric acid*, 50.0 g. (0.48 mole) of *malonic acid*, and approximately 120 ml. (about 1.5 moles) of *isobutylene* (Note 2), which is liquefied by passage into a large test tube immersed in a Dry Ice-acetone bath. The bottle is closed with a rubber stopper which is clamped or wired securely in place (Note 3) and is shaken mechanically at room temperature until the suspended *malonic acid* dissolves (Note 4). The bottle is chilled in an ice-salt bath and opened; then the contents are poured into a separatory funnel containing 250 ml. of water, 70 g. of *sodium hydroxide*, and 250 g. of ice. The mixture is shaken (carefully at first), the layers are separated, and the aqueous portion is extracted with two 75-ml. portions of *ether*. The organic layers are combined, dried over anhydrous *potassium carbonate*, and filtered into a dropping funnel attached to the neck of a 125-ml. modified Claisen flask (Note 5). The flask is immersed in an oil bath at about 100°, and the excess *isobutylene* and *ether* are removed by flash distillation effected by allowing the solution to run in slowly from the dropping funnel. The dropping funnel is then removed, and the residue is distilled at reduced pressure. The fraction boiling at 112–115°/31 mm. is collected. The yield of colorless *di-tert-butyl malonate* is 60.0–62.0 g. (58–60%), n_D^{25} 1.4158–1.4161, freezing point –5.9 to –6.1° (Note 6) and (Note 7).

2. Notes

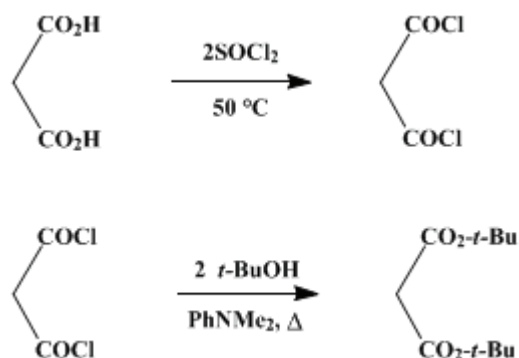
- Increase in the concentrations of reactants and product by elimination of the solvent shifts the equilibrium to the right and thus increases the yield of ester. In several runs by the checkers in which the described procedure was followed except that *ether* was omitted, *isobutylene* was increased to 240 ml. (3 moles), and shaking was continued for 12–15 hours to effect solution, yields of 88–91% were obtained. When *ether* was used as solvent, the larger amount of *isobutylene* raised the yield to only 73%. The submitters, however, have found that in the procedure without solvent the yield is more variable (in the range 69–92%), complete solution of the acid sometimes fails to occur, and in runs requiring long shaking for complete solution there is formed a lower-boiling substance the separation of which requires fractional distillation. Without solvent, there is usually an exothermic reaction as the mixture warms up. In the size run described this is no disadvantage, but in larger runs the heat evolved might be sufficient to cause the reaction to get out of control.
- Technical grade *isobutylene* supplied by the Matheson Company was used.
- The pressure during reaction on this scale does not exceed 40 p.s.i.
- Solution is usually complete within 6 hours, but sometimes as long as 12 hours may be required.
- The flask should be carefully washed with alkali before rinsing and drying, to ensure the removal of traces of acid which will catalyze the decomposition of the ester on warming to give *isobutylene*, *carbon dioxide*, and *acetic acid*. Once this decomposition begins, as evidenced by severe foaming, it is auto-catalyzed (by the *acetic acid* formed) and cannot be prevented from continuing at an accelerated rate except by rewashing the product and apparatus with alkali. The addition of some solid *potassium*

carbonate or magnesium oxide before distillation has been used with some *tert*-butyl esters to aid in inhibiting incipient decomposition. This treatment, however, does not appear to be necessary in the present preparation.

6. This preparation has been carried out by H. C. Dehm on a larger scale. From 150 g. of malonic acid, 200 ml. of ether, 10 ml. of concentrated sulfuric acid, and 375 ml. of isobutylene, there was obtained after shaking for 22 hours in a 1-l. bottle 201.3 g. (64% yield) of ester, $n_D^{24.2}$ 1.4161.

7. Other esters that have been prepared by this general procedure are: *tert*-butyl acetate, 50% yield, b.p. 94–97°/738 mm., n_D^{25} 1.3820; *tert*-butyl chloroacetate, 63% yield, b.p. 56–57°/16–17 mm., n_D^{25} 1.4204–1.4210 (carried out by R. C. Hunt); *tert*-butyl bromoacetate, 65% yield, b.p. 74–76°/25 mm., n_D^{25} 1.4162; *tert*-butyl α -chloropropionate, yield 63%, b.p. 52–53°/12 mm., n_D^{25} 1.4163 (carried out by J. S. Belew); *tert*-butyl *o*-benzoylbenzoate, 70% yield, m.p. 65–69°; di-*tert*-butyl succinate (dioxane was used instead of ether as solvent), 52% yield, b.p. 105–107°/7 mm., m.p. 31.5–35°; di-*tert*-butyl glutarate, 60% yield, b.p. 113–119°/9 mm., n_D^{25} 1.4215; di-*tert*-butyl β,β -dimethylglutarate, 67% yield, b.p. 72–75°/1 mm., n_D^{25} 1.4246.

[II. ACID CHLORIDE METHOD]



Submitted by Chittaranjan Raha²

Checked by William S. Johnson and Rudolph W. Kluiber.

1. Procedure

A. *Malonyl dichloride*. In a 250-ml. Erlenmeyer flask (Note 1) fitted by a ground-glass joint to a reflux condenser capped with a calcium chloride drying tube are placed 52 g. (0.5 mole) of finely powdered, dry malonic acid (Note 2) and 120 ml. (about 1.65 mole) of thionyl chloride (Note 3). The flask is warmed for 3 days in a heating bath kept at 45–50° (Note 4). During this period the mixture, which is agitated occasionally by gentle swirling, gradually darkens to a deep brownish red or sometimes a blue color. Finally the mixture is heated at 60° for 5–6 hours. After cooling, it is transferred to a 125-ml. modified Claisen flask and distilled at reduced pressure (water aspirator). A calcium chloride guard tube is inserted between the vacuum line and the apparatus, and the flask is heated with a bath rather than a free flame. After a small fore-run of thionyl chloride, the malonyl chloride distils at 58–60°/28 mm. The pale yellow product amounts to 50.5–60 g. (72–85% yield), n_D^{29} 1.4572.

B. *Di-tert-butyl malonate*. A 1-l. three-necked flask is fitted with a thermometer, a mercury- or rubber sleeve-sealed mechanical stirrer, a reflux condenser protected by a calcium chloride guard tube, and a dropping funnel (either pressure-equalized or protected by a calcium chloride guard tube). A mixture of 100 ml. (about 1 mole) of *tert*-butyl alcohol, dried by distillation from sodium (p. 134, Note 2), and 80 ml. (0.63 mole) of dry dimethylaniline (Note 5) is placed in the flask, the stirrer is started, and a solution of 28.0 g. (0.2 mole) of malonyl dichloride in about 60 ml. of dry, alcohol-free chloroform (Note 6) is added slowly from the dropping funnel while the reaction flask is cooled in an ice bath. The reaction is strongly exothermic, and the rate of dropping is regulated so that the temperature of the mixture does not exceed 30°. After the addition is complete (about 30 minutes) the light-greenish mixture is heated under reflux for 4 hours. The mixture is then cooled, 150 ml. of ice-cold 6*N* sulfuric acid is added with stirring, and the product is extracted with three 250-ml. portions of ether (Note 7). The combined ether extracts are washed once with 6*N* sulfuric acid, twice with water, twice

with 10% potassium carbonate, and once with saturated sodium chloride, and are finally dried over anhydrous sodium sulfate to which a small amount of potassium carbonate is added. The ether is removed by distillation at reduced pressure (water aspirator), and the residue (to which a pinch of magnesium oxide is added) is distilled at reduced pressure from a modified Claisen flask (Note 8). The yield of colorless di-*tert*-butyl malonate, distilling at 65–67°/1 mm., 110–111°/22 mm., is 35.8–36.2 g. (83–84%), n_D^{25} 1.4159, m.p. about –6°.

2. Notes

1. Better results are obtained by using a flat-bottomed flask, which permits the insoluble malonic acid to be distributed over a greater surface.
2. The reaction mixture is heterogeneous at first, and if the acid is not finely powdered, some of it remains unreacted. Attempts to carry out the reaction on a larger scale resulted in some charring and lower yields.
3. Eastman Kodak Company white label quality thionyl chloride is satisfactory.
4. The temperature range is critical, and yields are lower if it is not controlled carefully. The use of pyridine as a catalyst is not recommended as it produces charring even after relatively short reaction periods.
5. J. T. Baker dimethylaniline (purified grade) is satisfactory without distillation.
6. The chloroform was dried over and distilled from anhydrous calcium chloride just before use.
7. The dimethylaniline may be recovered from the aqueous layer where it is dissolved as the salt.
8. Di-*tert*-butyl malonate, like most *tert*-butyl esters, decomposes readily on heating in the presence of traces of acids. It is therefore desirable to give all glassware to be used for distillation of the material an alkali rinse before use. The addition of a small amount of magnesium oxide also helps to inhibit the decomposition during distillation.³ When decomposition starts, foaming is generally observed. In this event the addition of glass wool to the distillation flask helps to keep the product from foaming over.

3. Discussion

Procedure I is a modification³ of the method of Altschul⁴ for preparing *tert*-butyl esters. Di-*tert*-butyl malonate also has been prepared by the reaction of malonyl dichloride and *tert*-butyl alcohol in the presence of a base,^{5,6} and by the reaction of carbon suboxide with *tert*-butyl alcohol.⁷ Procedure II is based on the former⁵ method and developed from studies initiated by P. C. Mukharji of the University College of Science and Technology, Calcutta.

Malonyl dichloride has been prepared from malonic acid and thionyl chloride,^{5,8,9,10,11,12} and from carbon suboxide and anhydrous hydrogen chloride.¹³ The present procedure is adapted from that of Staudinger and Bereza¹⁰ and of Backer and Homan.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 417
- Org. Syn. Coll. Vol. 6, 414
- Org. Syn. Coll. Vol. 7, 142

References and Notes

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4. Altschul, *J. Am. Chem. Soc.*, **68**, 2605 (1946).
5. Backer and Homan, *Rec. trav. chim.*, **58**, 1048 (1939).
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8. Auger, *Ann. chim. et phys.*, [6] **22**, 347 (1891).

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 10. Staudinger and Bereza, *Ber.*, **41**, 4463 (1908).
 11. von Auwers and Schmidt, *Ber.*, **46**, 477 (1913).
 12. McMaster and Ahmann, *J. Am. Chem. Soc.*, **50**, 145 (1928).
 13. Diels and Wolf, *Ber.*, **39**, 696 (1906).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

carbon suboxide

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

thionyl chloride (7719-09-7)

chloroform (67-66-3)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

carbon dioxide (124-38-9)

pyridine (110-86-1)

sodium (13966-32-0)

dimethylaniline (121-69-7)

Malonyl dichloride (1663-67-8)

Malonic acid (141-82-2)

dioxane (5703-46-8)

magnesium oxide

isobutylene (9003-27-4)

tert-butyl alcohol (75-65-0)

tert-Butyl acetate (540-88-5)

tert-Butyl chloroacetate (107-59-5)

Di-tert-butyl malonate,
Malonic acid, di-t-butyl ester (541-16-2)

tert-butyl bromoacetate (5292-43-3)

tert-butyl α -chloropropionate (40058-88-6)

tert-butyl o-benzoylbenzoate

di-tert-butyl succinate (926-26-1)

di-tert-butyl glutarate (43052-39-7)

di-tert-butyl β,β -dimethylglutarate